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Synthesis of 3-methyleneindan-1-ol scaffold from modified Baylis–Hillman adduct: tandem Pd-catalyzed 5-*exo*-*trig* cyclization and iodide ion-assisted formal δ-carbon elimination/decarboxylation

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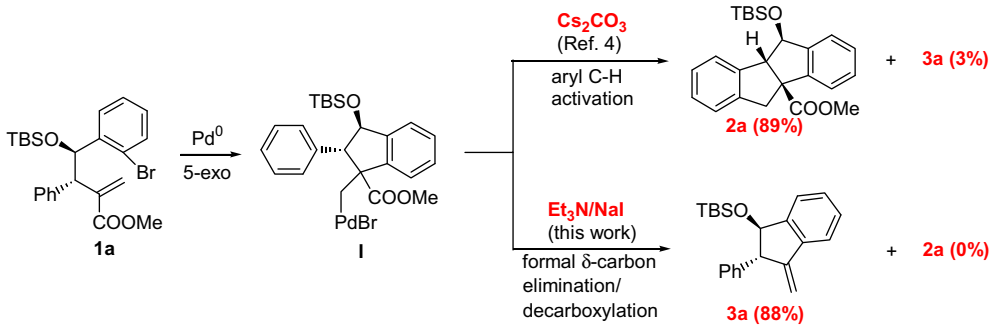
ABSTRACT

An efficient synthetic method of 3-methyleneindan-1-ol scaffold was developed from Baylis–Hillman adducts. The reaction involved palladium-catalyzed 5-*exo*-*trig* cyclization and iodide ion-assisted formal δ-carbon elimination/decarboxylation process.

Palladium-catalyzed domino reactions coupled with suitably designed substrates allow for the rapid establishment of complex molecules.[1] Chemical transformations of Baylis–Hillman adducts have received much attention during the last two decades.[2–4] Various cyclic and acyclic compounds have been synthesized by a variety of chemical transformations,[2–4] including a palladium-catalyzed reaction of suitably modified Baylis–Hillman adducts.[2i,3,4]

Recently, we reported a Pd-catalyzed domino reaction of acrylate derivative **1a**, prepared from Baylis–Hillman adduct via an indium-mediated Barbier type reaction, to form an indeno[2,1-*a*]indane **2a** (Scheme 1).[4] This compound was formed by selective 5-*exo*-*trig*-carbopalladation and aryl C–H activation cascade. In the reaction, a trace amount of methyleneindane **3a** (3%) was formed together via a formal δ-carbon elimination and concomitant decarboxylation.[4,5,7]

Synthesis of 3-alkylideneindan-1-ol derivatives has received much attention due to their usefulness as synthetic intermediates.[6] We assumed that methyleneindane **3a** could be formed as a major product by suppressing the aryl C–H activation process using a weak base such as Et_3N instead of Cs_2CO_3.[5,7] At the same time, the yield of **3a** could be increased by promoting the formal δ-carbon elimination



Scheme 1.

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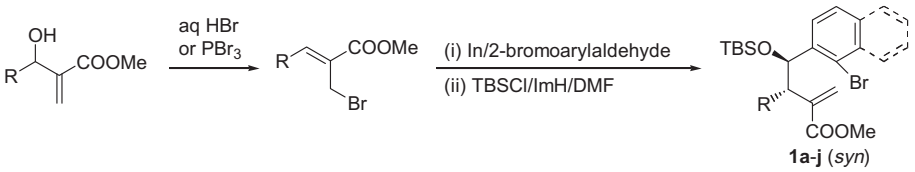
Table 1
Optimization of reaction conditions for the synthesis of **3a** from **1a**

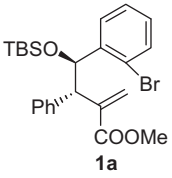
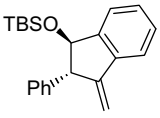
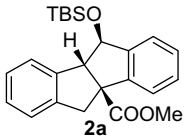
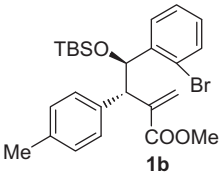
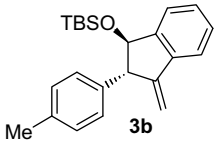
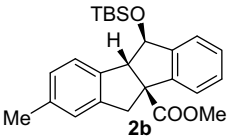
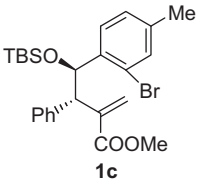
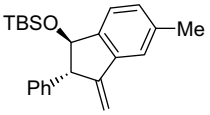
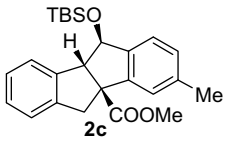
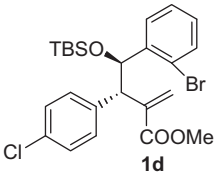
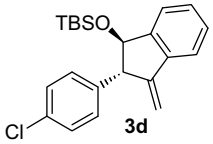
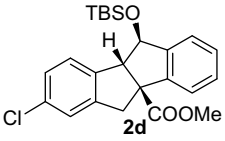
Entry	Conditions[a]	**2a**[b] (%)	**3a**[b] (%)
1[c]	Cs_2CO_3 (2.0 equiv), DMF, 110 °C, 1 h	89	3
2	Et_3N (2.0 equiv), DMF, 120 °C, 2 h	28	65
3	*i*-Pr_2NEt (2.0 equiv), TBAI (1.0 equiv), DMF, 120 °C, 2 h	45	50
4[d]	Et_3N (2.0 equiv), TBAI (1.0 equiv), DMF, 120 °C, 12 h	64	12
5	**Et_3N (2.0 equiv), NaI (1.0 equiv), DMF, 120 °C, 6 h**	**0**	**88**
6	Et_3N (2.0 equiv), NaCl (1.0 equiv), DMF, 120 °C, 2 h	37	59
7	no Et_3N, NaI (10 equiv), DMF, 120 °C, 4 h	0	0

[a] $Pd(OAc)_2$ (5 mol %) and PPh_3 (10 mol %) are common.
[b] Isolated yield.
[c] Ref. 4: $Pd(OAc)_2$ (10 mol %) and PPh_3 (20 mol %) were used.
[d] Without PPh_3.



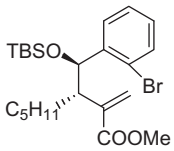
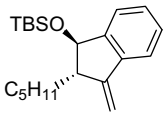
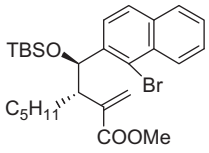
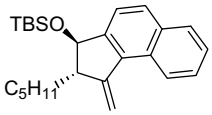
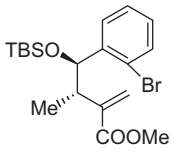
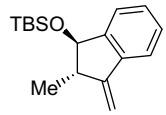
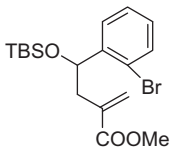
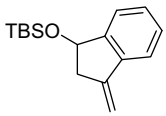
Scheme 2. R = Ph, 4-MePh, 4-ClPh, *n*-pentyl, Me, H, $Ph_2C{=}CH–$, $PhCH{=}C(Me)–$ (See Tables 2–4 for R and 2-bromoarylaldehyde of **1a–j**).

Table 2
Synthesis of methyleneindanes **3a–d**

Entry	Substrate	Products[a] (%)		
1	 **1a**	 **3a**	A:[b] 3 B:[c] 65 C:[d] **88**	 **2a** 89 28 **0**
2	 **1b**	 **3b**	A:[b] 5 B:[c] 62 C:[d] **84**	 **2b** 88 30 **0**
3	 **1c**	 **3c**	A:[b] 6 B:[c] 60 C:[d] **81**	 **2c** 86 35 **0**
4	 **1d**	 **3d**	A:[b] 4 B:[c] 60 C:[d] **86**	 **2d** 87 35 **0**

[a] Isolated yields.
[b] Results in Ref. 4 for comparision in the presence of Cs_2CO_3.
[c] Conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (2.0 equiv), DMF, 120 °C, 2 h.
[d] Conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (2.0 equiv), NaI (1.0 equiv), DMF, 120 °C, 6 h.

Table 3
Synthesis of methyleneindanes **3e–h**

Entry	Substrate	Products[a] (%)
1	 **1e**	 **3e** B:[b,c] 68 C:[d] **84**
2	 **1f**	 **3f** B:[b,c] 62 C:[d] **82**
3	 **1g**	 **3g** B:[b] not tried C:[d] **86**
4	 **1h**	 **3h** B:[b] not tried C:[d] **81**

[a] Isolated yields.
[b] Conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (2.0 equiv), DMF, 120 °C, 6 h.
[c] Some intractable side products were formed including dihydronaphthalene 4.
[d] Conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (2.0 equiv), NaI (1.0 equiv), DMF, 120 °C, 6 h.

and concomitant decarboxylation process.[4,5,7] The presence of a highly nucleophilic species such as an iodide ion in the reaction mixture would be helpful for the formation of a palladacycle intermediate (**III**, vide infra) and eventually could increase the yield of **3a**.[8,9] Actually, the yield of **3a** increased to 88% when we carried out the reaction in the presence of Et_3N/NaI, as shown in Scheme 1. Under the reaction conditions, indenoindane **2a** was not formed in any trace amount.

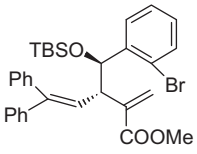
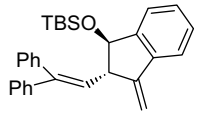
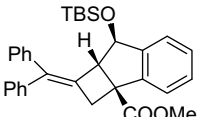
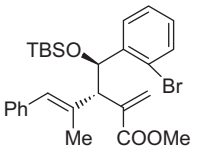
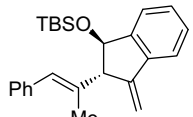
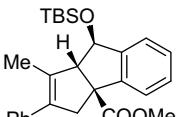
At the outset of our experiments, we carried out the reaction of **1a** under various conditions, as summarized in Table 1. As expected, the use of Et_3N changed the ratio of **2a**/**3a** dramatically (entry 2) as compared to the previous result employing Cs_2CO_3 (entry 1).[4] *N,N*-Diisopropylethylamine produced almost equal amounts of **2a** and **3a** (entry 3). The use of tetrabutylammonium iodide was not effective (entry 4). The best result was observed in the presence of Et_3N and NaI (entry 5). Sodium chloride was not effective (entry 6), and no reaction was observed without Et_3N (entry 7).

Encouraged by the results, various starting materials **1a–j** (*syn*) were prepared from the corresponding bromides of Baylis–Hillman adducts via an indium-mediated Barbier type reaction and a following protection of the alcohol moiety with *tert*-butyldimethylsilyl chloride according to the previous reports,[4,7,10] as shown in Scheme 2.

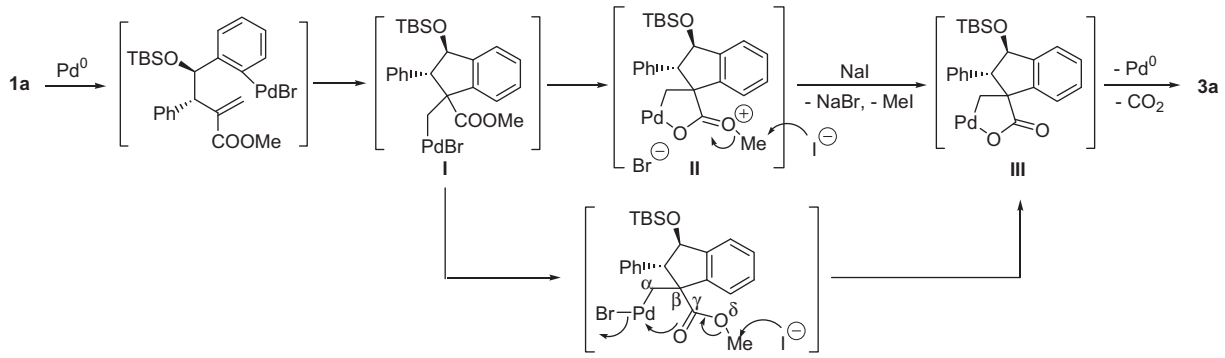
The syntheses of methyleneindanes **3b–d** were carried out via a Pd-catalyzed reaction with aryl-substituted substrates **1b–d**, as summarized in Table 2.[10] We conducted the reactions under the influence of Et_3N with and without NaI, in order to compare the effect of an iodide ion. As observed in all the cases, a combined use of Et_3N/NaI was superior to the system employing Et_3N alone. 2-Aryl-3-methyleneindan-1-ol derivatives **3b–d** were isolated in high yields (81–86%) as the sole products under the optimized conditions.

As a next experiment, we carried out the synthesis of 2-alkyl-3-methyleneindanes **3e–h**, and the results are summarized in Table 3. For the alkyl-substituted substrates **1e–g** and un-substituted **1h**, the conditions of Et_3N/NaI also showed better results than the conditions of Et_3N alone. The yields of **3e–h** were also excellent (81–86%) under the optimized conditions.

Table 4
Synthesis of methyleneindanes **3i** and **3j**

Entry	Substrate	Products[a] (%)	
1	 **1i**	 **3i** A:[b] 14 B:[c] 71 C:[d] **86**	 **4** 77 18 **0**
2	 **1j**	 **3j** A:[b] 12 B:[c] 57 C:[d] **82**	 **5** 85 22 **0**

[a] Isolated yields.
[b] Results in Ref. 7 for comparison in the presence of Cs_2CO_3.
[c] Results in Ref. 4 for comparison in the presence of Et_3N.
[d] Conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (2.0 equiv), NaI (1.0 equiv), DMF, 120 °C, 6 h.



Scheme 3.

As a last trial, we examined the selective synthesis of 2-alkenyl-3-methyleneindane derivatives **3i** and **3j** from **1i** and **1j**, as summarized in Table 4. Recently, we reported a novel synthesis of cyclobuta[*a*]indene **4** (77%) and cyclopenta[*a*]indene **5** (85%) by a Pd-catalyzed cyclization reaction under the influence of Cs_2CO_3 from **1i** and **1j**, respectively.[7] We also examined the reactions in the presence of Et_3N; however, the yields of **3i** and **3j** were moderate (57–71%).[7] The yields of **3i** and **3j** increased under the present optimized conditions employing NaI to 86% and 82%, respectively.

The mechanism for the formation of methyleneindane **3a** from **1a** could be proposed, as shown in Scheme 3. Oxidative addition of Pd^0 to the C–Br bond of **1a** and the following 5-*exo*-*trig*-carbopalladation generated an alkylpalladium intermediate **I**. The intermediate **I** could form an oxonium ion intermediate **II** via the interaction with nearby ester moiety.[8] A highly nucleophilic iodide ion may facilitate the formations of both **II** and **III**. Five-membered palladacycle intermediate **III** furnished **3a** by disruption with the elimination of CO_2 and regeneration of Pd^0. The formation of **III** could occur via a concerted mechanism from an alkylpalladium intermediate **I** involving a bond cleavage between an oxygen atom (δ-position) and a methyl group, as also shown in Scheme 3.[9] However, this point is not clear at this stage whether the conversion of **I** to **III** is concerted or stepwise.

We used TBS derivatives **1a–j** as starting materials in every entry.[11] The TBS group could be easily removed by treatment with TBAF.[4] As an example, compound **3g** was converted to 2-methyl-3-methyleneindan-1-ol (**6**) almost quantitatively (97%, TBAF, THF, rt, 1 h).

In summary, an efficient synthetic method of 3-methyleneindan-1-ol scaffold was developed from Baylis–Hillman adducts. The reaction involved a palladium-catalyzed 5-*exo*-*trig* cyclization and an iodide ion-assisted formal δ-carbon elimination/decarboxylation process. The latter process was mostly effective under the influence of Et_3N and NaI.

Acknowledgments

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10. *Typical procedure for the synthesis of compound* ***1e***: To a stirred solution of methyl (2*Z*)-2-(bromomethyl)oct-2-enoate[12] (125 mg, 0.5 mmol) and 2-bromobenzaldehyde (102 mg, 0.55 mmol) in aqueous THF (1:1, 1.5 mL) was added indium powder (63 mg, 0.55 mmol), and the reaction mixture was stirred at room temperature for 1 h. After the usual aqueous workup and column chromatographic purification process (hexanes/EtOAc, 10:1) the corresponding homoallyl alcohol was obtained, 134 mg (*syn*, 75%) and 14 mg (*anti*, 8%) as colorless oils. A solution of *syn*-homoallyl alcohol (107 mg, 0.3 mmol), TBSCl (90 mg, 0.6 mmol), and imidazole (61 mg, 0.9 mmol) in DMF

(1.0 mL) was stirred at room temperature for 12 h under nitrogen atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/Et_2O, 50:1) compound **1e** was obtained as colorless oil, 127 mg (90%). Other starting materials **1a–j** were prepared similarly,[4,7] and the selected spectroscopic data of unknown compounds **1e–h** are as follows.

Compound ***1e***: 90%; colorless oil; IR (film) 2953, 2857, 1723, 1463, 1256 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.29 (s, 3H), 0.02 (s, 3H), 0.77–0.97 (m, 12H), 1.06–1.32 (m, 6H), 1.51–1.62 (m, 1H), 1.71–1.85 (m, 1H), 2.97–3.09 (m, 1H), 3.63 (s, 3H), 5.04 (d, J = 6.6 Hz, 1H), 5.52 (d, J = 0.6 Hz, 1H), 6.23 (s, 1H), 7.02–7.07 (m, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.42 (dd, J = 7.8 and 1.2 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.04, −4.89, 14.05, 18.03, 22.49, 25.79, 26.72, 28.83, 31.87, 47.63, 51.64, 75.05, 122.43, 126.78, 127.16, 128.49, 130.02, 132.17, 139.35, 142.65, 167.80; ESIMS m/z 491 $[M+Na]^+$, 493 $[M+Na+2]^+$. Anal. Calcd for $C_{23}H_{37}BrO_3Si$: C, 58.83; H, 7.94. Found: C, 58.98; H, 8.02.

Compound ***1f***: 90%; colorless oil; IR (film) 2954, 2930, 2857, 1723, 1257, 1076 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.31 (s, 3H), 0.06 (s, 3H), 0.81–0.86 (m, 12H), 1.04–1.26 (m, 6H), 1.59–1.71 (m, 1H), 1.79–1.87 (m, 1H), 3.08–3.15 (m, 1H), 3.55 (s, 3H), 5.38 (d, J = 6.9 Hz, 1H), 5.53 (s, 1H), 6.18 (d, J = 0.9 Hz, 1H), 7.47–7.59 (m, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.74–7.80 (m, 2H), 8.32 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.97, −4.85, 14.03, 18.06, 22.51, 25.81, 26.81, 29.14, 31.90, 48.08, 51.57, 76.00, 122.14, 126.33, 126.91, 126.98, 127.06, 127.26, 127.82, 127.97, 131.84, 133.96, 139.23, 140.85, 167.70; ESIMS m/z 541 $[M+Na]^+$, 543 $[M+Na+2]^+$. Anal. Calcd for $C_{27}H_{39}BrO_3Si$: C, 62.41; H, 7.57. Found: C, 62.65; H, 7.42.

Compound ***1g***: 88%; colorless oil; IR (film) 2953, 2931, 2857, 1723, 1466, 1259 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 3H), 0.26 (s, 3H), 1.14 (s, 9H), 1.33 (d, J = 7.2 Hz, 3H), 3.43–3.51 (m, 1H), 3.99 (s, 3H), 5.41 (d, J = 4.8 Hz, 1H), 5.90 (t, J = 1.2 Hz, 1H), 6.55 (s, 1H), 7.36 (ddd, J = 7.5, 7.5 and 1.8 Hz, 1H), 7.53–7.58 (m, 1H), 7.75 (dd, J = 8.1 and 1.5 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.20, −4.94, 13.76, 18.07, 25.81, 40.20, 51.65, 74.27, 121.84, 126.55, 126.61, 128.48, 129.91, 132.38, 141.90, 142.57, 167.66; ESIMS m/z 435 $[M+Na]^+$, 437 $[M+Na+2]^+$. Anal. Calcd for $C_{19}H_{29}BrO_3Si$: C, 55.20; H, 7.07. Found: C, 55.51; H, 7.23.

Compound ***1h***: 85%; colorless oil; IR (film) 2953, 2931, 2857, 1726, 1631, 1468 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.26 (s, 3H), −0.09 (s, 3H), 0.77 (s, 9H), 2.49 (ddd, J = 13.2, 8.1 and 0.9 Hz, 1H), 2.63 (ddd, J = 13.2, 4.5 and 1.2 Hz, 1H), 3.65 (s, 3H), 5.18 (dd, J = 8.1 and 4.5 Hz, 1H), 5.42–5.43 (m, 1H), 6.13 (d, J = 1.5 Hz, 1H), 6.98–7.03 (m, 1H), 7.18–7.25 (m, 1H), 7.39 (dd, J = 8.1 and 1.2 Hz, 1H), 7.47 (dd, J = 7.8 and 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.88, −4.71, 18.37, 26.03, 42.09, 52.03, 72.46, 121.74, 127.63, 128.60, 128.81, 132.47, 136.84, 144.18, 167.79 (one carbon is overlapped); ESIMS m/z 421 $[M+Na]^+$, 423 $[M+Na+2]^+$. Anal. Calcd for $C_{18}H_{27}BrO_3Si$: C, 54.13; H, 6.81. Found: C, 54.19; H, 6.64.

Typical procedure for the synthesis of compound ***3a***: A solution of **1a**[4] (143 mg, 0.3 mmol), $Pd(OAc)_2$ (3 mg, 5 mol%), PPh_3 (8 mg, 10 mol%), triethylamine (61 mg, 0.6 mmol) and NaI (45 mg, 0.3 mmol) in DMF (1.0 mL) was stirred at 120 °C for 6 h under nitrogen atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/Et_2O 50:1) compound **3a** was obtained as colorless oil, 89 mg (88%).[4] Other compounds **3b–j**[4,7] were synthesized similarly, and the selected spectroscopic data of unknown compounds **3e–h** and **6** are as follows.

Compound ***3e***: 84%; colorless oil; IR (film) 2955, 2929, 2858, 1465, 1254, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 3H), 0.03 (s, 3H), 0.70–0.85 (m, 12H), 1.09–1.36 (m, 6H), 1.45–1.55 (m, 2H), 2.61–2.68 (m, 1H), 4.81 (d, J = 3.6 Hz, 1H), 4.85 (d, J = 2.4 Hz, 1H), 5.40 (d, J = 2.4 Hz, 1H), 7.10–7.16 (m, 2H), 7.17–7.23 (m, 1H), 7.31–7.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.03, −3.86, 14.10, 18.14, 22.59, 25.92, 26.06, 31.73, 32.30, 53.77, 79.08, 103.58, 120.60, 125.22, 128.22, 128.62, 140.08, 146.12, 150.48; ESIMS m/z 331 $[M+H]^+$. Anal. Calcd for $C_{21}H_{34}OSi$: C, 76.30; H, 10.37. Found: C, 76.53; H, 10.16.

Compound ***3f***: 82%; colorless oil; IR (film) 2955, 2929, 2857, 1463, 1254, 1108 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 3H), 0.21 (s, 3H), 0.81–1.00 (m, 12H), 1.19–1.50 (m, 6H), 1.65–1.72 (m, 2H), 2.83–2.89 (m, 1H), 4.98 (d, J = 3.6 Hz, 1H), 5.30 (d, J = 1.8 Hz, 1H), 5.92 (d, J = 2.1 Hz, 1H), 7.44–7.57 (m, 3H), 7.76 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.98, −3.90, 14.11, 18.19, 22.61, 25.93, 26.38, 31.64, 32.28, 55.94, 78.89, 107.89, 122.95, 124.46, 125.54, 126.86, 129.03, 129.35, 129.64, 134.19, 134.80, 145.24, 150.81; ESIMS m/z 381 $[M+H]^+$. Anal. Calcd for $C_{25}H_{36}OSi$: C, 78.89; H, 9.53. Found: C, 78.74; H, 9.49.

Compound ***3g***: 86%; white solid, mp 48–49 °C; IR (KBr) 2958, 2930, 2857, 1464, 1256, 1106 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 3H), 0.21 (s, 3H), 0.96 (s, 9H), 1.32 (d, J = 6.9 Hz, 3H), 2.75–2.85 (m, 1H), 4.77 (d, J = 5.4 Hz, 1H), 4.96 (d, J = 2.4 Hz, 1H), 5.47 (d, J = 2.7 Hz, 1H), 7.23–7.29 (m, 2H), 7.30–7.35 (m, 1H), 7.45–7.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.06, −4.03, 16.26, 18.10, 25.90, 49.12, 81.33, 102.51, 120.50, 124.53, 128.05, 128.71, 139.44, 146.07, 151.39; ESIMS m/z 275 $[M+H]^+$. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.71; H, 9.34.

Compound ***3h***: 81%; colorless oil; IR (film) 2954, 2930, 2857, 1646, 1468, 1358, 1255 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 3H), 0.18 (s, 3H), 0.95 (s, 9H), 2.62–2.71 (m, 1H), 3.12 (dddd, J = 16.2, 7.2, 1.8 and 1.8 Hz, 1H), 5.03 (dd, J = 1.8 and 1.8 Hz, 1H), 5.30 (dd, J = 7.2 and 5.4 Hz, 1H), 5.46 (dd, J = 2.7 and 1.8 Hz, 1H), 7.24–7.29 (m, 2H), 7.30–7.39 (m, 1H), 7.46–7.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.60, −4.38, 18.25, 25.90, 43.29, 73.67, 103.32, 120.41, 124.85, 128.13, 128.67, 139.73, 146.50, 147.61; ESIMS m/z 261 $[M+H]^+$. Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.83; H, 9.01.

Compound ***6***: 97%; white solid, mp 106–107 °C; IR (KBr) 3345, 2960, 2859, 1642, 1466, 1327, 1046 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, J = 6.9 Hz, 3H), 1.96 (br s, 1H), 2.70–2.81 (m, 1H), 4.75 (s, 1H), 5.01 (d, J = 2.1 Hz, 1H), 5.51 (d, J = 2.7 Hz, 1H), 7.28–7.34 (m, 2H), 7.41–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.56, 49.50, 81.05, 103.25, 120.69, 124.56, 128.65, 128.96, 139.63, 145.24, 151.13; ESIMS m/z 161 $[M+H]^+$. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.18; H, 7.43.

11. The use of TBS-protected starting materials was crucial for the effective reaction. When we use the corresponding acetate derivative instead of **1a**, both 5-*exo-trig* and 6-*endo-trig* carbopalladation compete, as previously observed.[4] In addition, the use alcohol derivatives directly without protection with TBS moiety showed the formation of intractable complex mixtures including γ-hydroxybutenolide.[4,7]

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